California Environmental Protection Agency

Air Resources Board

COMPARISON OF THREE-POINT CALIBRATION AND SINGLE-POINT CALIBRATION RESULTS FOR 1,3-BUTADIENE AND BENZENE IN AMBIENT AIR SAMPLES ANALYZED BY METHOD MLD051

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1. Purpose

The Organics Laboratory Section proposes a change in the quantitation procedure used in the Method MLD051 Standard Operating Procedure (SOP). Method MLD051 is used to determine 1,3-butadiene and benzene in ambient air. The new procedure would replace the current 1-point Response Factor with a 3-point calibration curve. The comparison data from a preliminary study of the 1-point and 3-point calibrations indicated that the 1-point standard curve underestimates 1,3-butadiene and benzene concentrations. The purpose of this study is to evaluate and compare the effects of 3-point calibration with respect to 1-point calibration on the analysis of ambient air samples for 1,3-butadiene and benzene by Method MLD051. The comparison of results obtained from ambient air samples will help define the relationship between historical values obtained with 1-point calibration, and future values obtained from 3-point calibration.

2. Background

The SOP for 1,3-butadiene analysis was first introduced in 1985 and the SOP for benzene analysis was approved in 1986. Since then, several modifications have been made to improve the precision and accuracy of the measurements of 1,3-butadiene and benzene concentration. In the last revision, made in 1997, the analyses of 1,3-butadiene and benzene were combined in the current Method MLD051, "Standard Operating Procedure for the Determination of 1,3-Butadiene and Benzene in Ambient Air by Capillary Column Gas Chromatography with Photoionization Detector," Revision 3.0.

The Standard Operating Procedures (SOP) governing analysis of 1,3-butadiene and benzene have been revised as gas chromatographic procedures and equipment have evolved and improved. Quantitation of a target analyte has, to date, used a 1-point Response Factor (RF) based on the analysis of a standard at a known concentration. The RF is calculated as shown below.

$$RF = \frac{\text{(Standard Concentration) * (Standard Volume)}}{\text{(Standard Area Counts)}}$$

The RF actually represents a two point linear curve, with one point determined by the standard response and concentration, and the second fixed at the origin (i.e., zero response and zero concentration).

The use of a 1-point RF is supported by the periodic performance of multi-point linearity studies where the target compounds are analyzed at five to seven different concentrations with three to five replicates at each concentration. This procedure verifies the linear range of the instrument/method and can be used to establish the Limit of Detection (LOD) for the target analytes.

The Laboratory is proposing a change in the quantitation procedure used in Method MLD051. The new procedure uses a 3-point standard curve, with a 2nd order least squares,

forced through the origin. Typical calibration curves for 1,3-butadiene and benzene are shown in Figures 1 and 2. The straight line represents the 1-point RF calibration from the high standard concentration through the origin. As shown, the 3-point curve yields higher concentration results per unit response for both compounds up to the high standard concentration.

3. Data

The results of analysis performed on ambient air samples from the Toxic Air Contaminant monitoring sites, including MATES II sites, submitted between July 16, 1998 and July 20, 1999 were used in this study. A total of 696 samples were received during that period. The samples were analyzed for benzene and 1,3-butadiene following the Laboratory's SOP for Method MLD051. The Method was modified to include two additional Standard concentration levels for each component. The low-level concentrations are the lowest calibration levels that can be achieved with the Varian gas chromatograph used in the analysis. The mid-level concentrations were chosen because they are close to the statewide average ambient concentrations. The concentration levels are listed below.

	CONCENTRATION	
	1,3-Butadiene [ppb]	**Benzene [ppb]**
Low Standard	**0.138**	**0.65**
Mid Standard	**0.275**	**1.3**
High Standard (1 Point Concentration)	**1.1**	**5.2**

After analysis, the data was quantitated twice, first using the 1-point RF, and second using the least squares fit of a 2nd order curve through all three standard points. The concentration data for all samples, by both quantitation methods, for both compounds was compiled and examined.

4. Data Analysis

The compiled data was examined for completeness. Of the 2784 individual data points, representing 1392 pairs of 1,3-butadiene and benzene results, 160 points were rejected. The number of points, listed by compound, and the reason for their rejection are given in Table 1. The remaining 2624 data points, 1276 for 1,3-butadiene and 1348 for benzene, were used to complete the data analysis.

Graphical examination of both 1,3-butadiene and benzene data showed good correlation between the 1-point RF based results and the 2nd order 3-point calibration curve based results. A mathematical comparison of the data was done using Microsoft Excel 97's Regression Data Analysis tool. A 3rd order least squares fit was performed on both the

1,3-butadiene data set and the benzene data set, using the 1-point RF based data as the independent variable, and the 3-point curve based data as the dependent variable. A 3rd order least squares fit was also performed on both data sets, using the 3-point curve based data as the independent variable, and the 1-point RF based data as the dependent variable. The 3rd order fit was chosen for the comparison because it provided a better fit for data at or near the LOD and high standard concentrations.

Charts showing the data values, the 3rd order least squares fitted lines, and the equations computed for the fitted lines are given in Figures 3 through 6 for all four data comparisons. Values for the LOD and high standard concentration, with a straight line through both points, are also included for reference.

The Percent Differences (% Differences) between the data using the 3-point curve calibration and the data using the 1-point RF calibration, for 1,3-butadiene and benzene respectively, were calculated. These % Difference values are plotted against the 3-point curve based data in Figures 7 and 8. As expected, the data shows the greatest difference at lower concentrations. This % Difference was calculated as shown below.

$$\text{\% Difference} = \frac{\text{(Actual 3-Point Curve Result) - (Actual 1-Point RF Results)}}{\text{(Actual 3-Point Curve Result)}}$$

To illustrate the difference between derived and direct results, the % Differences between the results calculated using the 3rd order least squares fit correlation equation for 1- to 3-point data applied to actual 1-point RF based data, and the 3-point calibration curve based data were calculated. This % Difference was calculated as shown below.

$$\text{\% Difference} = \frac{\text{(Calculated 3-Point Result) - (Actual 3-Point Curve Result)}}{\text{(Actual 3-Point Curve Result)}}$$

The same calculation was made using the results calculated using the 3rd order least squares fit correlation equation for 3- to 1-point data applied to actual 3-point curve based data, and the 1-point RF based data. This % Difference was calculated as shown below.

$$\text{\% Difference} = \frac{\text{(Calculated 1-Point Result) - (Actual 1-Point Curve Result)}}{\text{(Actual 1-Point Curve Result)}}$$

These % Difference results are plotted in Figures 9 and 10. To allow plotting of 1,3-butadiene and benzene data on the same scale, the concentrations were normalized to the maximum concentration obtained for each compound. A vertical line showing the approximate 5 X LOD concentration level is included for reference. Examination of the % Difference results yields the following observations.

When converting 1-point data to 3-point data:

1,3-butadiene
- 96.9% of the calculated concentrations are within ± 10% of the actual concentrations;
- 99.8% of the calculated concentrations are within ± 15 % of the actual concentrations;

Benzene
- 95.0 % of the calculated concentrations are within ± 10% of the actual concentrations;
- 99.6% of the calculated concentrations are within ± 15 % of the actual concentrations.

When converting 3-point data to 1-point data:

1,3-butadiene
- 96.1% of the calculated concentrations are within ± 10% of the actual concentrations;
- 98.9% of the calculated concentrations are within ± 15 % of the actual concentrations;

Benzene
- 93.9 % of the calculated concentrations are within ± 10% of the actual concentrations;
- 99.0% of the calculated concentrations are within ± 15 % of the actual concentrations.

5. Conclusions

Bias

The positive bias shown in the results of the analysis of ambient air samples for benzene and 1,3-butadiene, using a 3-point, 2^{nd} order, least squares fitted calibration, rather than a 1-point RF based calibration, are as expected. The calibration curves in Figures 1 and 2 graphically demonstrate that at a given response, within the calibration range (i.e., the origin through the high standard concentration), the 1-point RF based result is lower than the 3-point calibration based result. The greatest Absolute Difference is in the mid-range, where the two response curves are furthest apart.

Correlation

Figures 3 through 6 illustrate that the 3^{rd} order correlation between the results obtained using a 3-point, 2^{nd} order, least squares fitted calibration, and those obtained with a 1-point RF based calibration is good for both compounds.

As shown in Figures 7 and 8, the Percent Difference between actual 3-point results and actual 1-point results with respect to actual 3-point results is very concentration dependent. It increases as the concentration decreases and approaches the Limit of Detection (LOD). The variability of this difference also increases as the concentration decreases. As the lower end of the calibration range and the LOD is approached, the precision of the analysis decreases which adds greater variability to the percent difference. Although the Absolute

Difference is greatest at mid range, the Percent Difference is greatest in the lower calibration range.

Figures 9 and 10 demonstrate that the concentrations of 1,3-butadiene and benzene, obtained from the analysis of ambient air samples by Method MLD051, can be converted using the correlation equations derived from this study. Whether converting 1-point data to 3-point data, or 3-point data to 1-point data, at least 98% of the derived results will be within ± 15% of the results calculated directly from the actual calibration curves. This is the same % Difference criterion that is applied to the analysis of control samples and duplicate samples under Method MLD051.

Conversion

Conversion of the 1,3-butadiene and benzene concentrations acquired using Method MLD051 with the correlation equations derived from this study is an acceptable means of temporarily offsetting the discontinuity in the historical data set caused by changing from a 1-point to a 3-point calibration procedure. This applies to the non-rejected data collected between July 16, 1998 and July 20, 1999.

Applying the correlation equations to data sets outside of the study period might be less satisfactory. Any data meeting the rejection conditions shown in Table 1 would not convert properly. The correlation equations are also dependent on the high standard concentration. If that value were different from the value used in this study, the coefficients for the correlation equations would be different and the resulting conversion would not be satisfactory.

Table 1: Rejected Data

Number of Data Points Rejected		Reason for Rejection
Benzene	1,3-Butadiene	
2	2	Invalid sample
22	22	Both benzene and 1,3-butadiene concentrations exceeded the high standard concentration
NA	32	1,3-Butadiene concentrations exceeded the high standard concentration
NA	18	QA Audits samples that did NOT CONTAIN 1,3-butadiene
NA	22	Atypical 1,3-butadiene results
20	20	Atypical benzene and 1,3-butadiene calibrations
44	116	Subtotal of Rejected Points, by Compound
160		Total of All Rejected Points (5.7 % of 2784 total points)

Explanation

Invalid Sample:	Results for samples that did not meet sampling constraints or suffered problems within the lab were rejected.
Results Exceed High Standard Conc.:	Sample results that exceed the high standard concentration are diluted and reanalyzed. If the dilution factor is known, the actual sample results, prior to applying the dilution factor, should lie within the distribution.
Atypical 1,3-Butadiene Results:	The 1,3-butadiene results from 4/13/99 followed a significantly different distribution than other results. This may have been caused by a PID lamp change for that day.
Atypical Calibrations:	The calibrations for both benzene and 1,3-butadiene, on 11/5/98, were unusual, and were traced to a PID lamp change. Results for this day followed a significantly different distribution than other results.

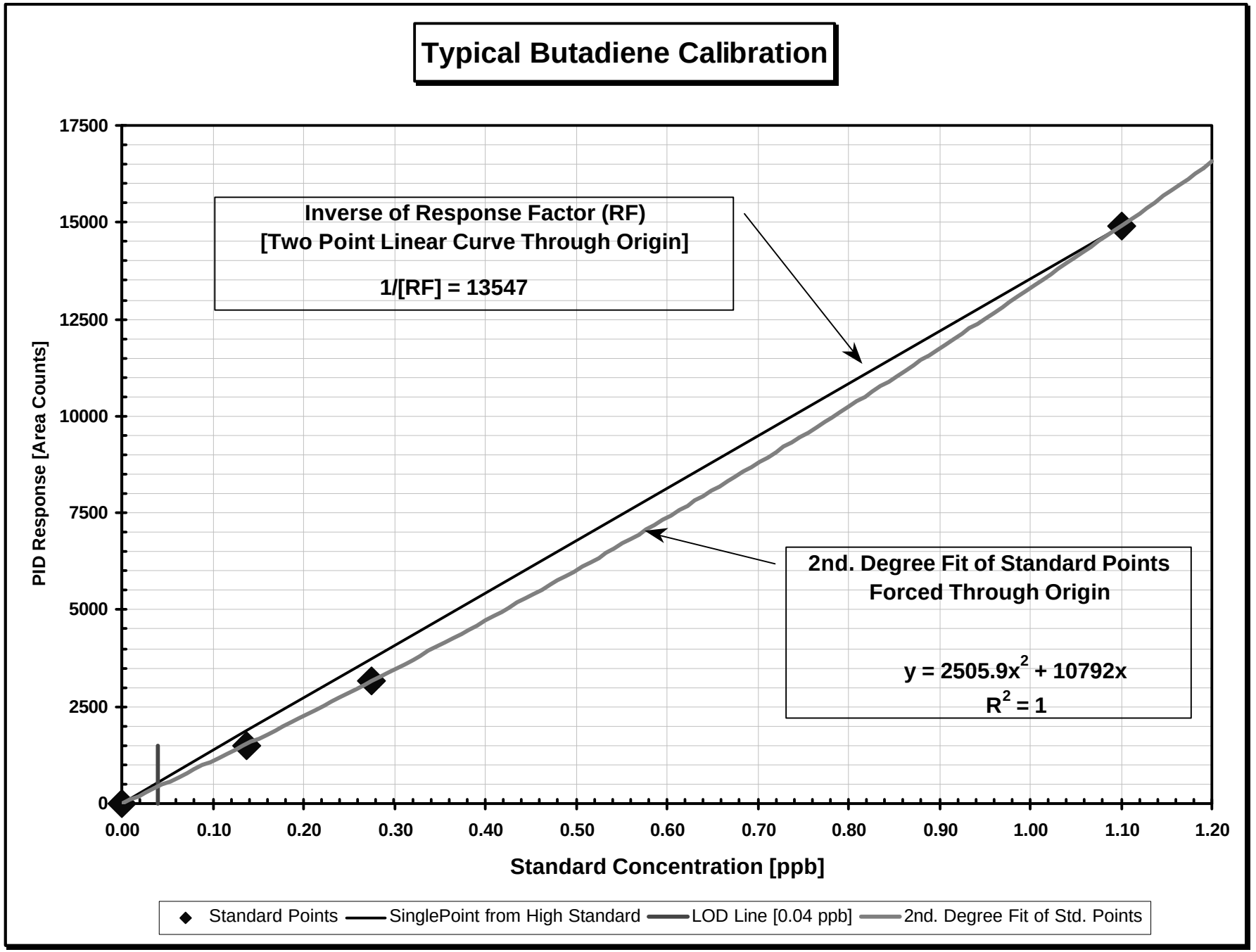

Typical Butadiene Calibration
Inverse of Response Factor (RF)
[Two Point Linear Curve Through Origin]
1/[RF] = 13547
2nd. Degree Fit of Standard Points
Forced Through Origin
y = 2505.9x2 + 10792x
R2 = 1
PID Response [Area Counts]
17500
15000
12500
10000
7500
5000
2500
0
0.00
0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80
0.90
1.00
1.10
1.20
Standard Concentration [ppb]
Standard Points
SinglePoint from High Standard
LOD Line [0.04 ppb]
2nd. Degree Fit of Std. Points

Figure 1

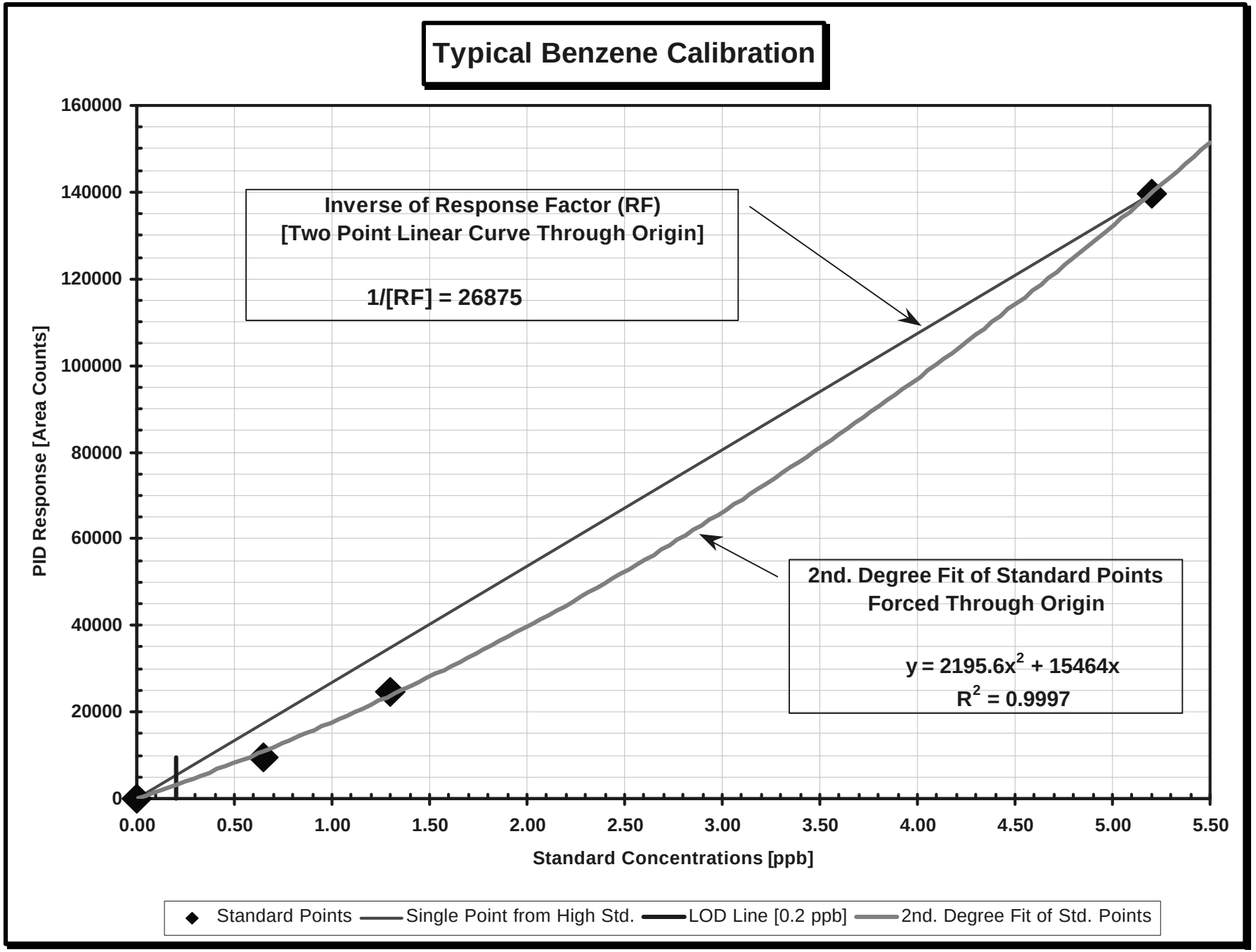

Typical Benzene Calibration
Inverse of Response Factor (RF)
[Two Point Linear Curve Through Origin]
1/[RF] = 26875
2nd. Degree Fit of Standard Points
Forced Through Origin
y = 2195.6x2 + 15464x
R2 = 0.9997
PID Response [Area Counts]
Standard Concentrations [ppb]
160000
140000
120000
100000
80000
60000
40000
20000
0
0.00
0.50
1.00
1.50
2.00
2.50
3.00
3.50
4.00
4.50
5.00
5.50
Standard Points
Single Point from High Std.
LOD Line [0.2 ppb]
2nd. Degree Fit of Std. Points

Figure 2

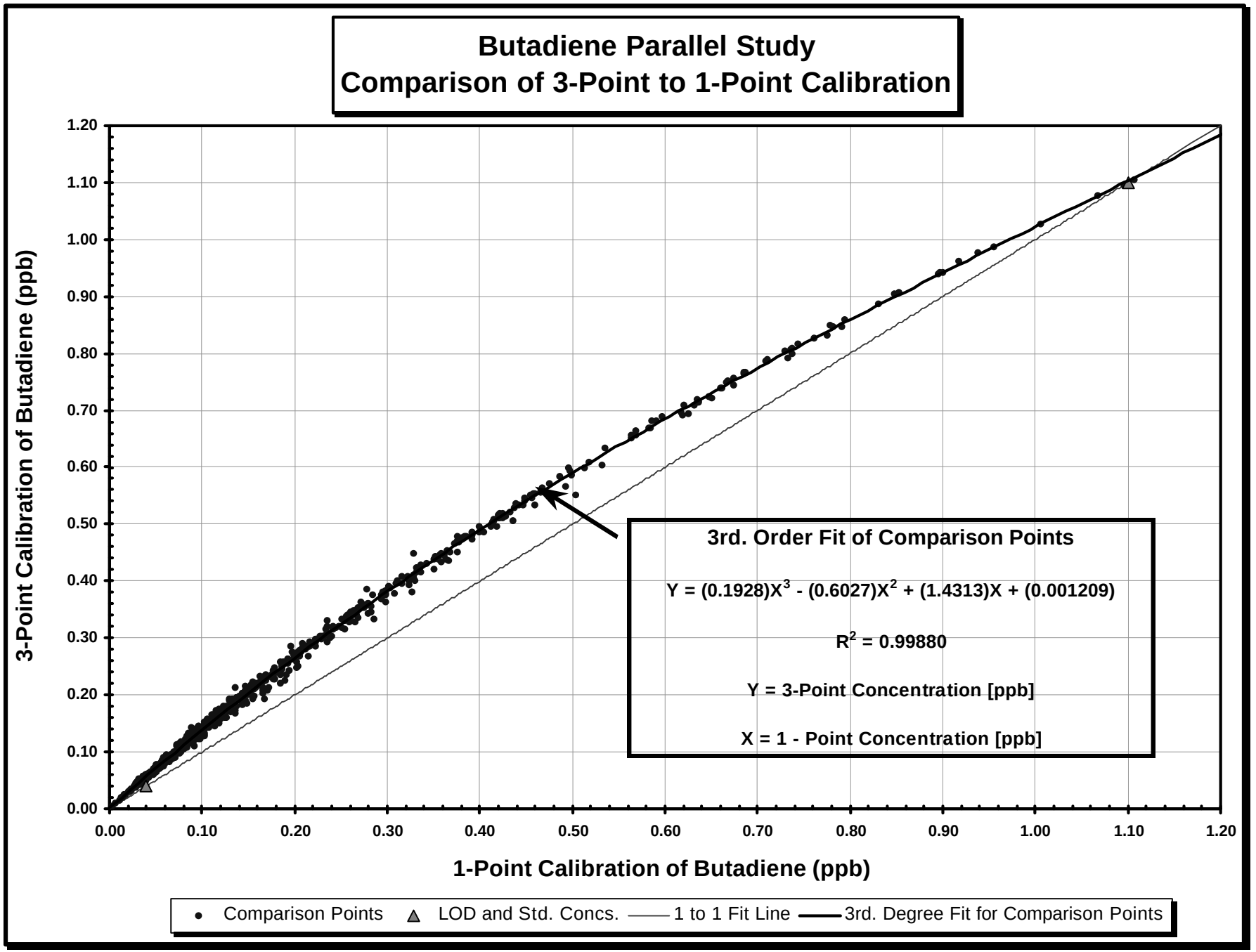

Butadiene Parallel Study
Comparison of 3-Point to 1-Point Calibration
3-Point Calibration of Butadiene (ppb)
1-Point Calibration of Butadiene (ppb)
0.00
0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80
0.90
1.00
1.10
1.20
3rd. Order Fit of Comparison Points
Y = (0.1928)X3 - (0.6027)X2 + (1.4313)X + (0.001209)
R2 = 0.99880
Y = 3-Point Concentration [ppb]
X = 1 - Point Concentration [ppb]
Comparison Points
LOD and Std. Concs.
1 to 1 Fit Line
3rd. Degree Fit for Comparison Points

Figure 3

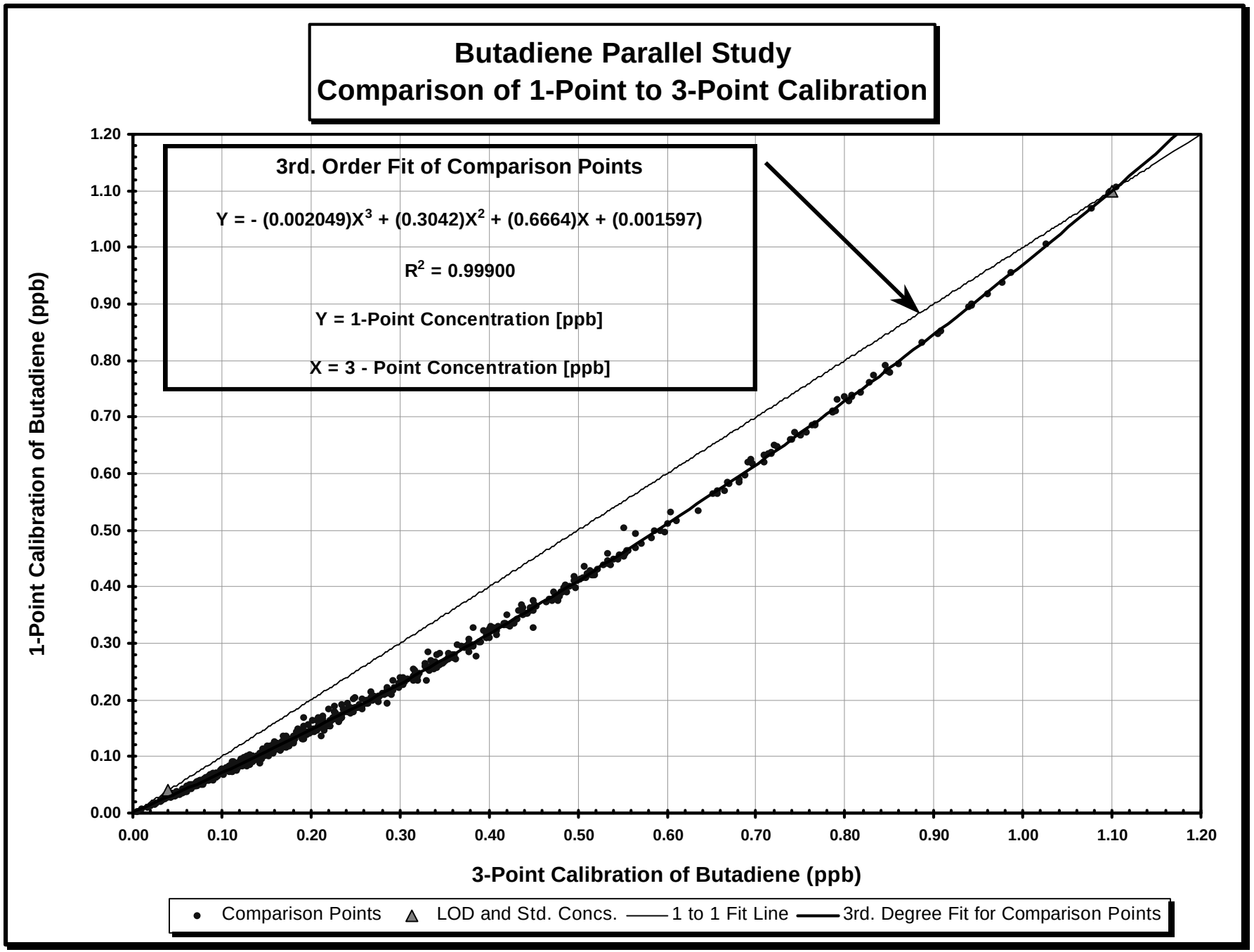

Butadiene Parallel Study
Comparison of 1-Point to 3-Point Calibration
3rd. Order Fit of Comparison Points
Y = - (0.002049)X3 + (0.3042)X2 + (0.6664)X + (0.001597)
R2 = 0.99900
Y = 1-Point Concentration [ppb]
X = 3 - Point Concentration [ppb]
1-Point Calibration of Butadiene (ppb)
3-Point Calibration of Butadiene (ppb)
0.00
0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80
0.90
1.00
1.10
1.20
Comparison Points
LOD and Std. Concs.
1 to 1 Fit Line
3rd. Degree Fit for Comparison Points

Figure 4

Figure 5

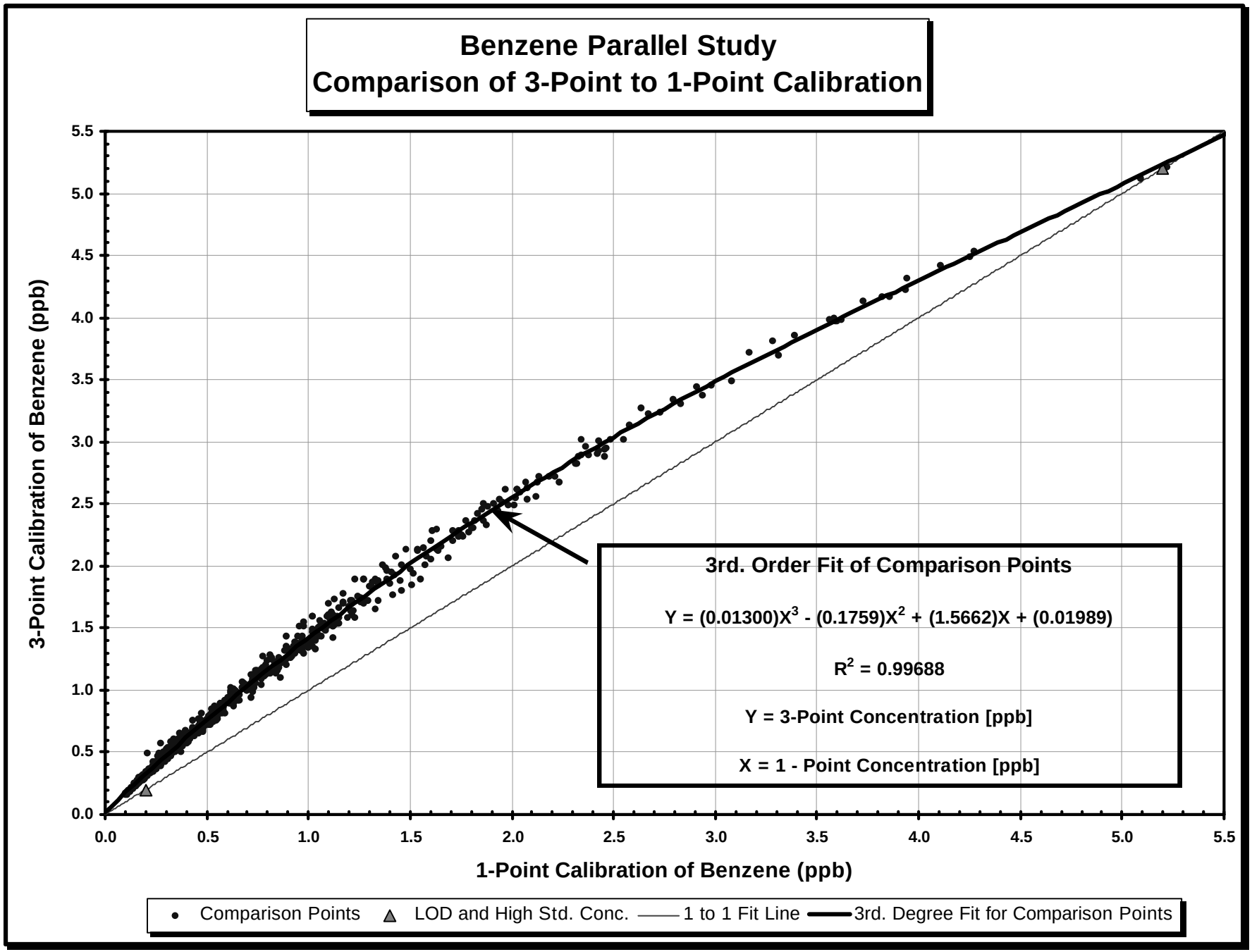
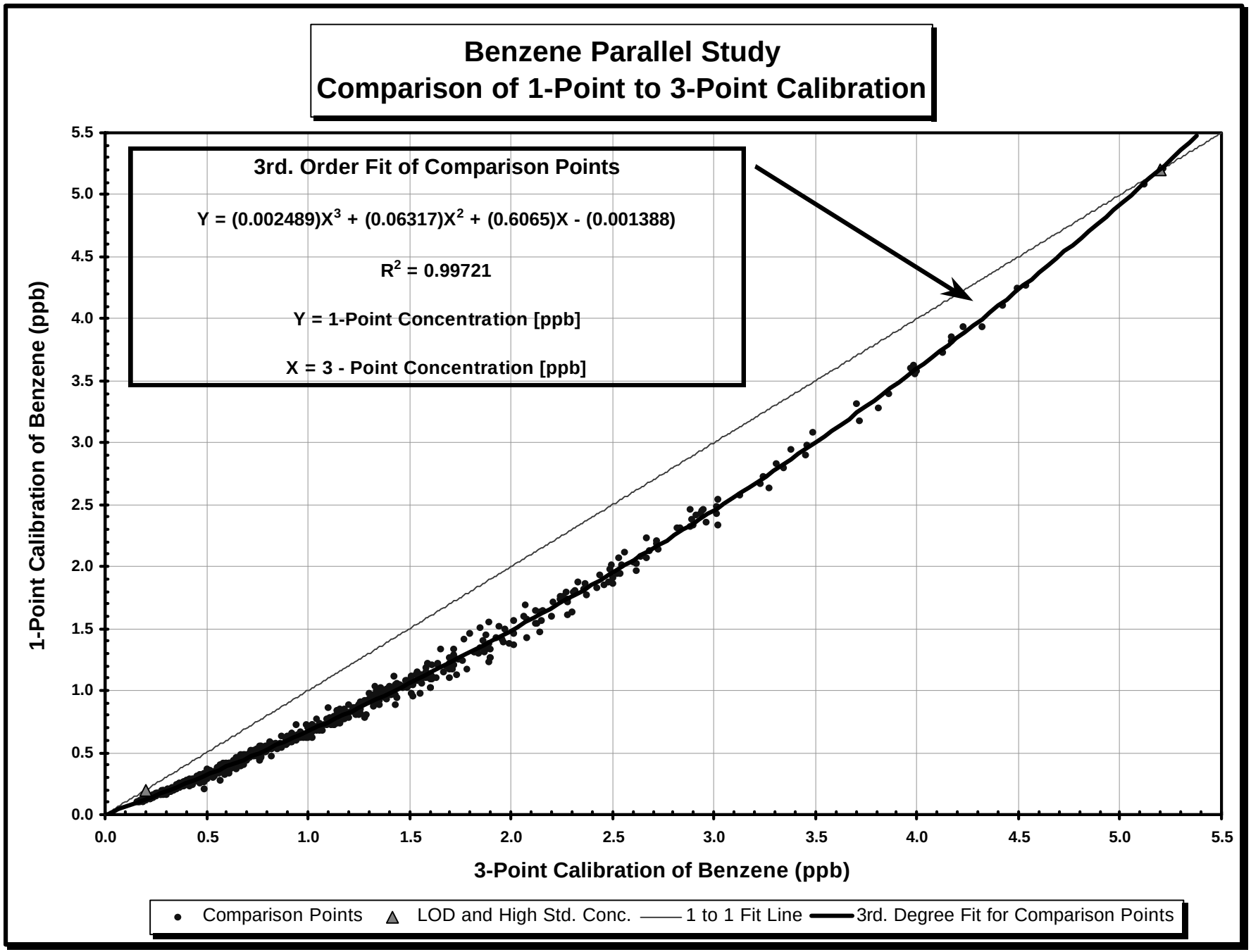

Benzene Parallel Study
Comparison of 3-Point to 1-Point Calibration
3-Point Calibration of Benzene (ppb)
1-Point Calibration of Benzene (ppb)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
3rd. Order Fit of Comparison Points
Y = (0.01300)X3 - (0.1759)X2 + (1.5662)X + (0.01989)
R2 = 0.99688
Y = 3-Point Concentration [ppb]
X = 1 - Point Concentration [ppb]
Comparison Points
LOD and High Std. Conc.
1 to 1 Fit Line
3rd. Degree Fit for Comparison Points

Figure 6


Benzene Parallel Study
Comparison of 1-Point to 3-Point Calibration
3rd. Order Fit of Comparison Points
Y = (0.002489)X3 + (0.06317)X2 + (0.6065)X - (0.001388)
R2 = 0.99721
Y = 1-Point Concentration [ppb]
X = 3 - Point Concentration [ppb]
1-Point Calibration of Benzene (ppb)
3-Point Calibration of Benzene (ppb)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
Comparison Points
LOD and High Std. Conc.
1 to 1 Fit Line
3rd. Degree Fit for Comparison Points

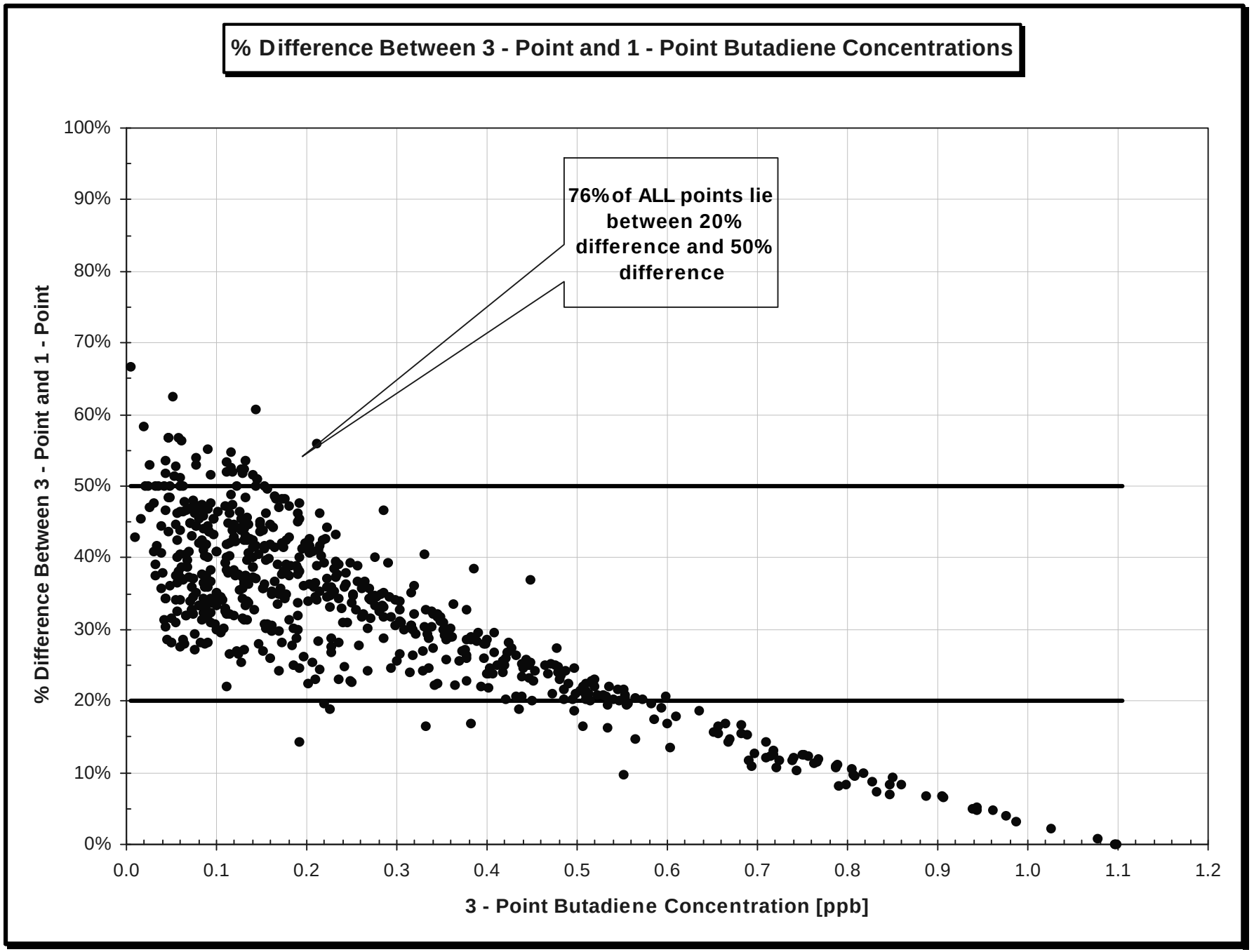

% Difference Between 3 - Point and 1 - Point Butadiene Concentrations
76% of ALL points lie between 20% difference and 50% difference
% Difference Between 3 - Point and 1 - Point
3 - Point Butadiene Concentration [ppb]
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2

Figure 7

Figure 8

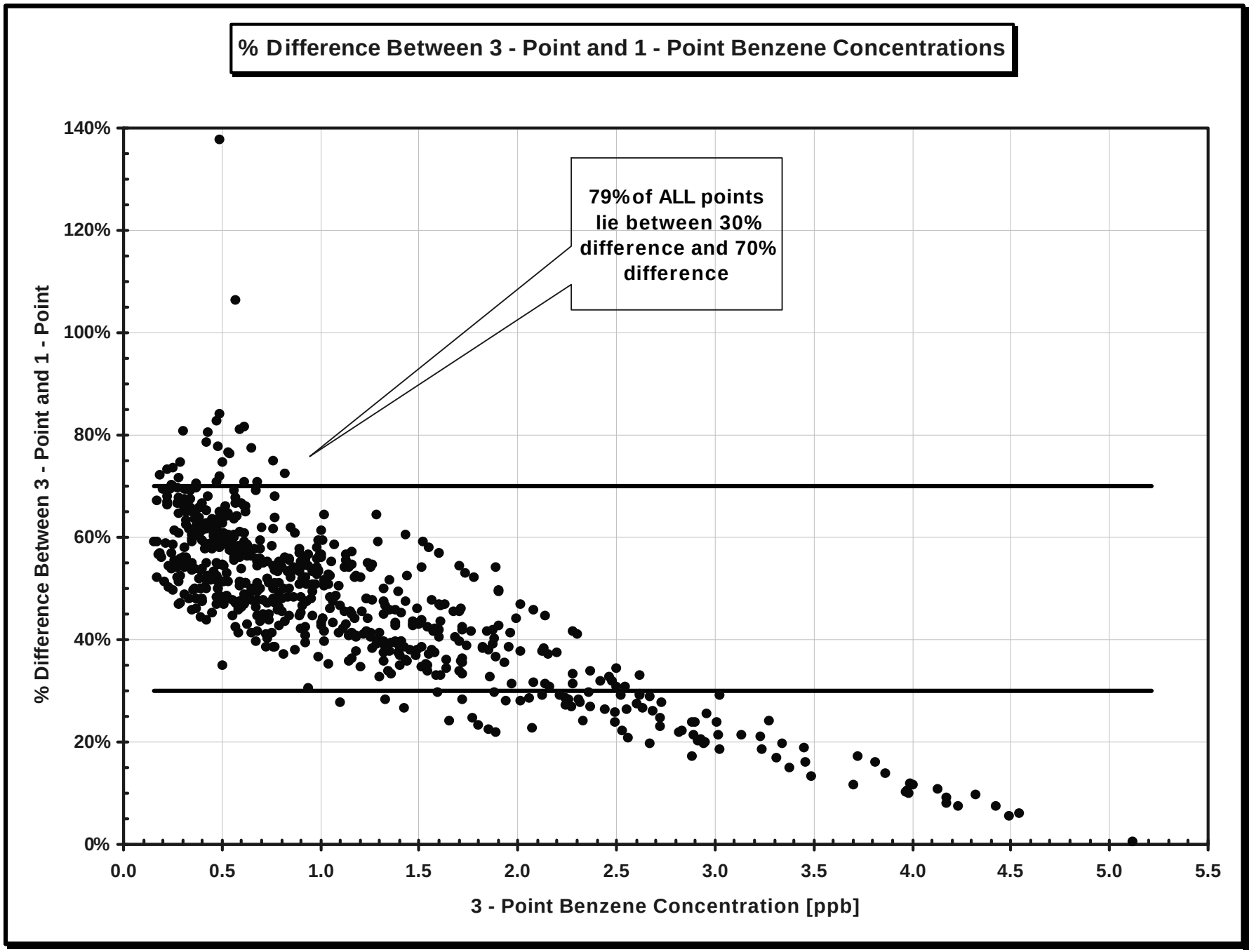
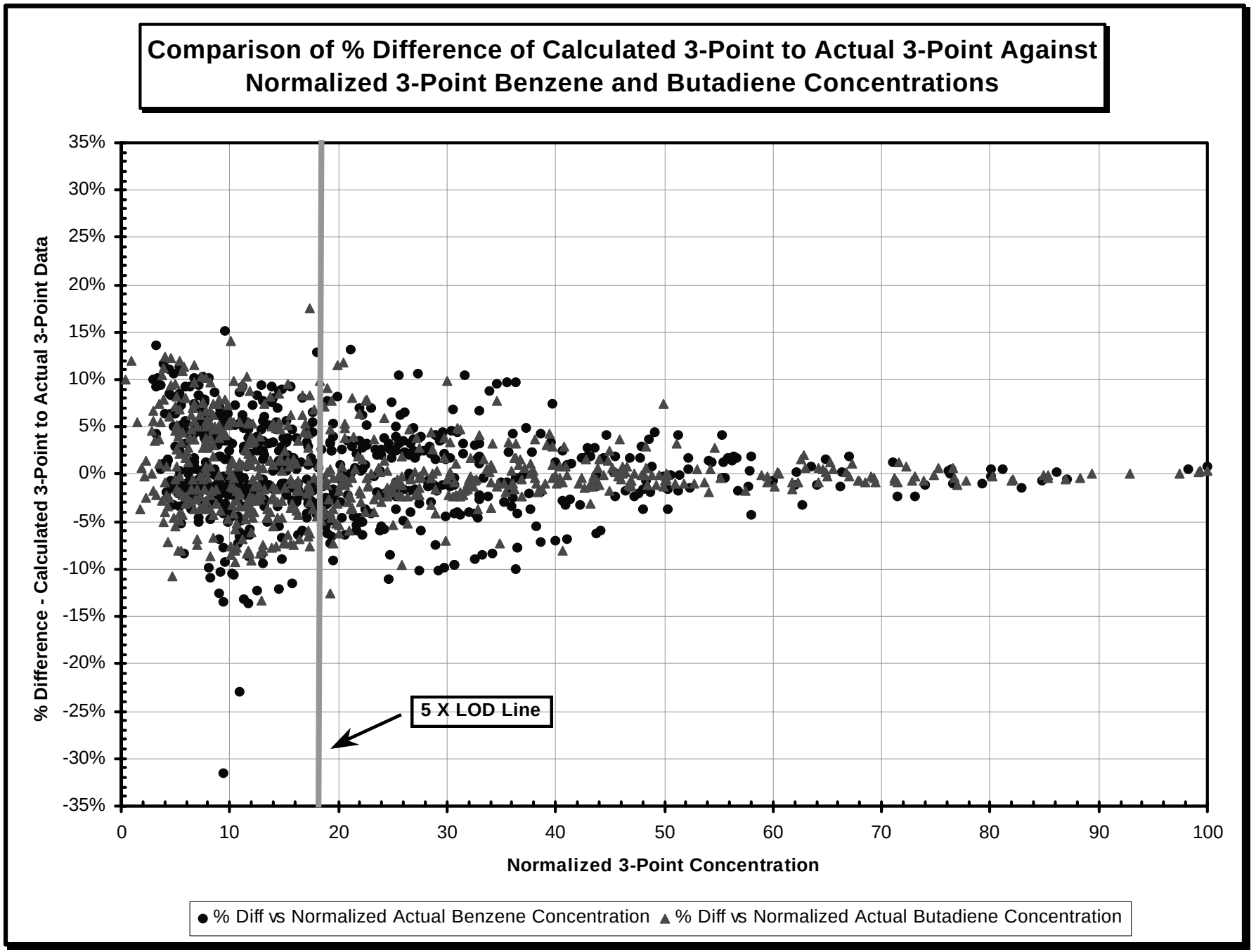

% Difference Between 3 - Point and 1 - Point Benzene Concentrations
79% of ALL points lie between 30% difference and 70% difference
% Difference Between 3 - Point and 1 - Point
140%
120%
100%
80%
60%
40%
20%
0%
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
3 - Point Benzene Concentration [ppb]

Figure 9


Comparison of % Difference of Calculated 3-Point to Actual 3-Point Against Normalized 3-Point Benzene and Butadiene Concentrations
% Difference - Calculated 3-Point to Actual 3-Point Data
35%
30%
25%
20%
15%
10%
5%
0%
-5%
-10%
-15%
-20%
-25%
-30%
-35%
0
10
20
30
40
50
60
70
80
90
100
Normalized 3-Point Concentration
5 X LOD Line
% Diff vs Normalized Actual Benzene Concentration
% Diff vs Normalized Actual Butadiene Concentration

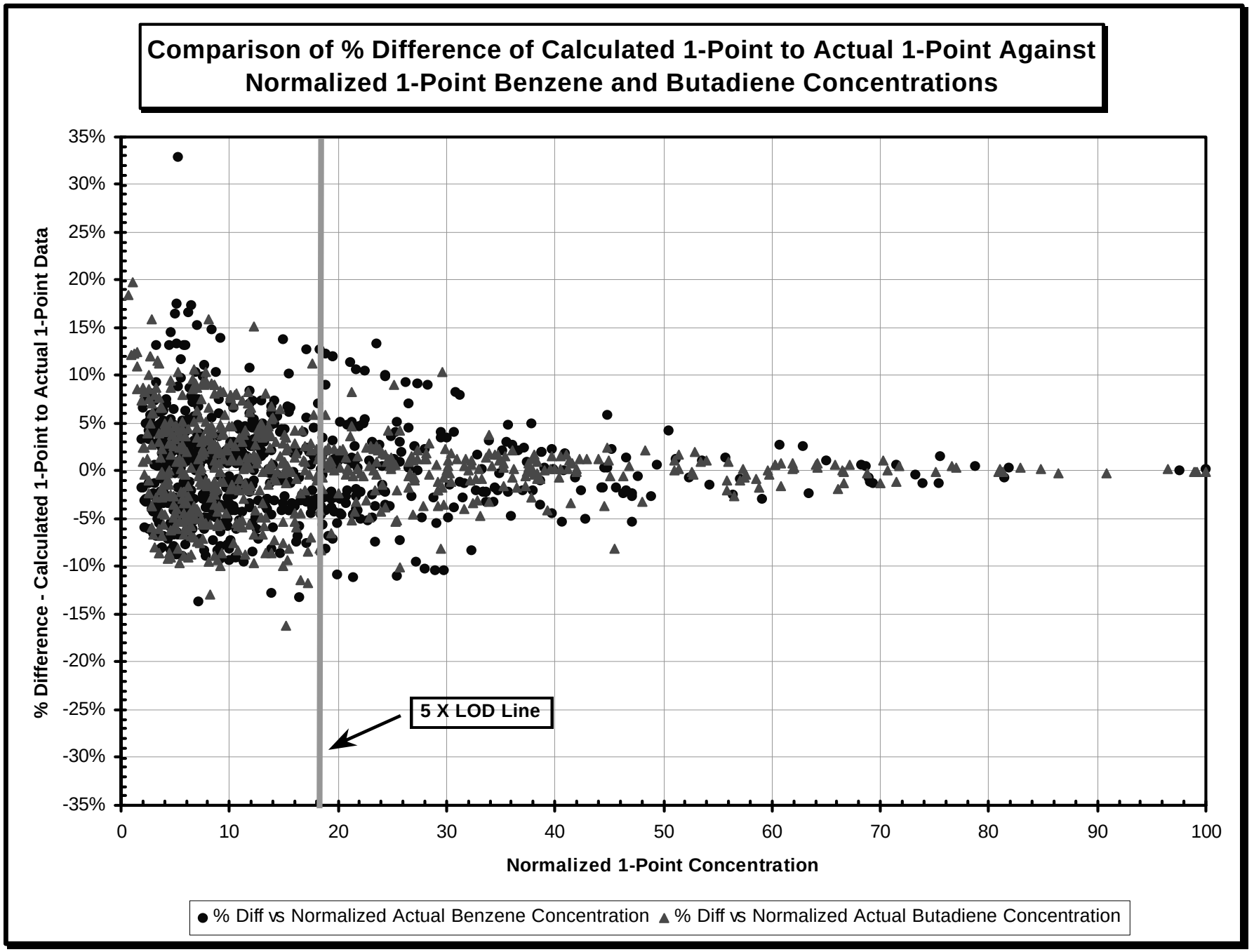

Comparison of % Difference of Calculated 1-Point to Actual 1-Point Against Normalized 1-Point Benzene and Butadiene Concentrations
% Difference - Calculated 1-Point to Actual 1-Point Data
35%
30%
25%
20%
15%
10%
5%
0%
-5%
-10%
-15%
-20%
-25%
-30%
-35%
0
10
20
30
40
50
60
70
80
90
100
Normalized 1-Point Concentration
5 X LOD Line
% Diff vs Normalized Actual Benzene Concentration
% Diff vs Normalized Actual Butadiene Concentration

Figure 10